1. Experimental Section

1.1. Synthesis of hollow sulfur spheres
Sulfur spheres were prepared via an aqueous solution process. Typically, sodium thiosulfate (Na$_2$S$_2$O$_3$, Aldrich) solution (100 mL, 9.64 mg/mL) was mixed with 100 mL of PVP (0.4 M, Aldrich, molecular weight of ~ 55000) under strong stirring for 30 min. Then, 0.8 mL of concentrated hydrochloric acid (HCl, Sinopharm Chemical Reagent Co., Ltd) was gradually added to the mixture under magnetic stirring for 2 h, resulting in the formation of hollow sulfur spheres.

1.2. Synthesis of boron-doped graphene quantum dots and BCS aerogel
Firstly, graphene quantum dots were prepared by precise cutting of graphene oxide sheets, which were produced by a modified Hummers’ method. In detail, graphene oxide sheets (30 mg) were dispersed in 50 mL of DMF under strong sonication. The obtained solution was transferred in a 100 mL Teflon-lined stainless steel autoclave and heated at 200 °C for 10 h. The obtained solution was filtered by a 0.22 μm microporous membrane, achieving the formation of oxygen-containing graphene quantum dots. 9 mg of H$_3$BO$_3$ was added into 60 mL of oxygen-containing graphene quantum dots (0.1
mg/mL) and the mixture was sonicated for 30 min before being transferred into a Teflon-lined stainless steel autoclave and reacted at 180 °C for 12 h, resulting in the formation of boron-doped graphene quantum dots. The prepared boron-doped graphene quantum dots (10 mL, 0.05 mg/mL) were dispersed with graphene oxide solution (50 mL, 2 mg/mL) under strong sonication, which results in the preparation of boron-doped carbon sheets. Sulfur spheres prepared above were mixed with this boron-doped carbon sheets with a mass ratio of 20:1 under stirring and sonication. The obtained mixture was freeze-dried under low vacuum less than 10 Pa, and further being treated with a vapor-reduction process with the assistance of hydrazine hydrate, and BCS aerogel with consecutive “core-shell” structures has been developed after a vacuum drying treatment.

1.3. Characterization

The morphologies and micro-structures of the prepared samples were recorded by a Field Emission Scanning Electron Microscopy (SEM) of Hitachi SU8010. And energy dispersive X-ray spectroscopy (EDS) images were captured with an equipment of EDAX PW9900. Thermogravimetric analysis (TGA) was conducted with TA 50 from room temperature to 800 °C. XRD patterns were recorded by a D8 Advanced XRD diffractometer (Bruker) with Cu Kα = 0.154056 nm. Raman spectroscopy of B-doped graphene sheets was recorded on a Renishaw inVia with 632.8 nm diode laser excitation on 1800-line grating. FTIR spectrum of graphene oxide was recorded based on a PERKIN ELMER FT-IR spectrometer in the range of 600-4000 cm⁻¹ using KBr pellet method. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo escalab 250 Xi equipment with a Al Kα (hv = 1486.6 eV).

1.4. Electrochemical measurement

BCS aerogel with a diameter of ~13 mm was directly used as working cathode for Li-S battery. A polypropylene (PP) membrane (Cellgard 2400) was utilized as the separator, and lithium foil was used as the anode. The columnar cells were assembled in a glove box filled in Ar with H₂O and O₂ contents less than 0.1 PPM. 1 M lithium
bis(trifluoromethane) sulfonamide (LiTFSI) in 1,3-dioxolane/dimethoxymethane (DOL/DME, 1:1 by volume) with 0.3 M LiNO₃ added. The amount of electrolyte used in each cell is about 40 μL. Galvanostatic discharge / charge curves were obtained with a LAND-CT2001A system at different current densities. Cyclic voltammetry (CV) tests were performed on an ARBIN electrochemistry workstation (MSTAT-5V/5mA, 32 channels) in a voltage window of 1.0 - 3.0 V vs Li⁺/Li. Electrochemical impedance spectroscopy (EIS) was performed on a Salartron - Princeton electrochemical workstation from 100 kHz to 0.01 kHz with an applied voltage amplitude of 10 mV. Pure sulfur spheres were mixed with super P (conductive additions) and polyvinylidene fluoride (PVDF) binder with a mass ratio of 8:1:1 in N-methylpyrrolidone (NMP), and the obtained slurry was coated on an aluminum foil and dried at 60 ºC for 12 h. Other tests were the same as that of BCS aerogel cathode.
Fig. S1 TEM image of graphene quantum dots.
Fig. S2 SEM image of the B-doped carbon sheets with size of dozens of micrometers.
Fig. S3 (a) SEM image of BCS aerogel and corresponding energy specta of (b) carbon, (c) sulfur and (d) boron elements.
Fig. S4 Energy spectrum of BCS aerogel and the weight percent of each elements.
Fig. S5 XRD patterns of sulfur spheres, BCS aerogel and graphene sheets.
Fig. S6 TGA curves of sulfur spheres, BCS aerogel and graphene sheets.
Fig. S7 FTIR spectrum of graphene oxide sheets.
**Fig. S8** (a) schematic model of the surface of graphene oxide sheets with oxygen-containing groups; (b) created pores on the surface of reduced graphene sheets.
**Fig. S9** BCS aerogel cathode can substitute the copper wire in a turn-on electrical circuit.
Fig. S10 Raman spectrum of reduced graphene sheets.
Fig. S11 CV curves of Li-S battery with pure sulfur sphere cathode for the first three cycles at 0.1 mV/s.
Fig. S12 Discharge/charge curves of Li-S battery with pure sulfur sphere cathode at 0.1 C.
Fig. S13 Schematic illustration of the rapid insertion / extraction of lithium ions throughout BCS aerogel.
Fig. S14 Nyquist plots of the Li-S batteries with BCS aerogel and pure sulfur cathodes after being cycled for 10 times.
Fig. S15 Equivalent circuit used for fitting the Nyquist plots of Li-S batteries with BCS aerogel and pure sulfur cathodes.
Fig. S16 Discharge/charge curves of Li-S battery with BCS aerogel cathode after being cycled for 500 times.
**Fig. S17** SEM image of BCS aerogel cathode disassembled from the Li-S cell which was cycled for 500 times.
Fig. S18 Nyquist plots of BCS aerogel cathode on the 1\textsuperscript{st} and 500\textsuperscript{th} cycles.
Fig. S19 Long-term cycling performance of pure sulfur cathode at 0.2 C.
Fig. S20 Discharge / charge curves of pure sulfur cathode on the 360 cycle.
Fig. S21 Long-term cycling performance of BCS aerogel cathode without the addition of LiNO$_3$. 

![Graph showing long-term cycling performance of BCS aerogel cathode without LiNO$_3$.]
Fig. S22 Comparison of the electrochemical performances of BCS aerogel cathode and the other (doped) carbon / sulfur cathodes.
Table S1. Impedance parameters calculated from the EIS curves based on the equivalent circuit.

<table>
<thead>
<tr>
<th>Li-S cathodes</th>
<th>$R_e$ (Ω)</th>
<th>$R_{et}$ (Ω)</th>
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<tbody>
<tr>
<td>BCS aerogel</td>
<td>2.8</td>
<td>27.2</td>
</tr>
<tr>
<td>Pure sulfur</td>
<td>4.9</td>
<td>51.9</td>
</tr>
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References